OFFICIAL DOCUMENT

Albuquerque Bernalillo County

Water Utility Department

WATER RECLAMATION DIVISION
4201 2ND STREET SW, ALBUQUERQUE, NEW MEXICO 87105

WATER QUALITY LABORATORY
STANDARD OPERATING PROCEDURE APPROVAL FORM

WQL SOP **502 Cold Vapor Mercury**

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MODIFICATIONS AND REASONS FOR REVISION

❖ **2006 A2LA Audit Requirements**
❖ **Deficiency 15; Changed Pg. 15 to show calculations of stock standards.**

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CITY OF ALBUQUERQUE

WATER QUALITY LABORATORY

STANDARD OPERATING PROCEDURE

PERKIN-ELMER FLOW INJECTION MERCURY SYSTEM (FIMS)

MERCURY COLD VAPOR ANALYSES

ORIGINAL ISSUE DATE :December 1997

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1.0 SCOPE & APPLICATION

1.1 This procedure measures "total" mercury (organic + inorganic) in drinking, surface, ground, industrial and domestic waste water, extracts of soil and sludge for dissolved, total recoverable, and suspended sample fractions.

1.2 The working range of this method using a Perkin Elmer Flow Injection Mercury System (FIMS) configured as in the following SOP is 0.5 to10 ug/L.

1.3 For reference where this method is approved for use in compliance monitoring programs consult the appropriate sections of the Code of Federal Regulations (40 CFR Part 136 Table 1B for NPDES, and Part 141 Section 141.23 for drinking water).

1.4 All mercury analyses will be conducted according to Method 3112A--Metals by Cold Vapor Atomic Absorption Spectrometry, Standard Methods for the Examination of Water and Wastewater 18th Edition.

2.0 SUMMARY OF PRINCIPLES & PROCEDURES

2.1 The Flow Injection/ Mercury Cold Vapor Technique

2.1.1 Principle of the Flow Injection Technique:

The central component of the Flow Injection System is the flow injection valve (FIAS-valve). The FIAS-valve injects a defined and reproducible sample volume into a carrier or reagent stream. The pump transports the carrier (and sample) and reagent streams to the manifold. In the manifold the various reagents mix and possibly react. The outflow from the manifold usually goes to a detection system.

2.1.2 Principle of the Mercury Cold Vapor Technique:

If a reagent solution is introduced at a suitable point in the flow injection system, the sample undergoes a chemical reaction as it is transported through the system. This procedure is used in FIMS applications.

The mercury must be in an ionic form in the sample solution. When the reducing agent ($SnCl_5$) mixes with the sample, the ionic mercury is converted to metallic mercury. An inert carrier gas (argon) transports the mercury to the spectrometer. A major advantage of the technique is the inherent separation of the analyte element from the matrix.

The first channel of pump 1 feeds a stream of carrier fluid (HCl) continuously through the FIAS-valve to the manifold.

With the FIAS-valve in the **Fill** position, pump 1 fills the sample loop. In the **Inject** position, the contents of the sample loop enter the carrier stream and are carried to the manifold, which acts as the reaction cell.

The second channel of pump 1 carries the reducing agent, $SnCl_2$, directly to the manifold. The sample (in the acidic carrier stream) and reductant mix in the manifold and a spontaneous reaction takes place, reducing the ionic mercury to metallic mercury.

The hydrogen is released and a stream of carrier gas carry the mercury vapor to the gas/liquid separator where the liquid is separated from the gaseous components. The liquid is pumped to waste by the third channel of pump 1. The gas phase continues on to the FIMS-cell, which is in the radiation beam of the spectrometer.

2.1.3 Stannous Chloride:

Used as the reductant for the determination of mercury. According to the type of matrix, the sample solution is treated so the mercury is present in ionic form. Residual organically bound mercury can be oxidized with potassium permanganate. Reductant is dispensed into the sample solution and mercury is reduced to the elemental state.

$$Hg^{2+} + Sn^{2+} \xrightarrow[KMnO_4,\ K_2S_2O_8]{} Hg + Sn^{4+}$$

Elemental mercury vapor is driven out of the sample solution by the carrier gas and is transported to the quartz cell where its absorption is measured. When the sample vapor is atomized in the cell, a peak absorption signal is produced over an integration read time, the height of which is proportional to the amount of analyte in the sample.

3.0 DEFINITION OF TERMS

3.1 Accuracy: Combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to a true value.

3.2 Analytical Batch: Samples which are analyzed together with the same method sequence and the same lots of reagents and with the same manipulations common to each sample within the same time period. The samples are of the same TYPE and the batch will be designated by sample type, protocol, revision#, year, the actual number of batches since the beginning of the current year, and sample collection beginning and ending dates. **A batch consist of 20 samples or less of the same WQL protocol.**

3.3 Calibration Blank (Cal Blk): A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to auto-zero the instrument.

3.4 Continuing Calibration Verification Standard (CCVS): A mid-range ICAL standard used to verify continuing calibration. CCVS standards are used to verify instrument performance on a daily basis.

3.5 Control Charts: Charts used to maintain a current awareness of the accuracy/precision of each method and that the default acceptance criteria in the methods be updated to properly reflect the capability of the laboratory.

3.6 Correlation Coefficient (CC): Is a number in the range -1 through +1 that measures how closely the calculated line fits the data. All calibration curves must have a calculated CC of greater than or equal to 0.995.

3.7 Carrier Gas: The gas, argon, used to transport mercury vapor or hydride to the measurement cell when using the FIAS.

3.8 Dissolved Analyte: The concentration of analyte in an aqueous sample that will pass through a 0.45 *u*m membrane filter.

3.9 Field Duplicate (FD): A field duplicate sample that is exposed to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of

the FD is to determine if method analytes or other interferences are present in the field.

3.10 Field Reagent Blank (FRB): An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.11 Initial Calibration Standard (ICAL): A solution prepared from the dilution of stock standard solutions. The ICAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.12 Initial Calibration Verification Standard (ICVS): A standard of known concentration obtained from an second source vendor, the same source but different lots, or the same lot prepared by a second analyst. ICVS standards are used to verify the calibration standards.

3.13 Instrument Detection Limit (IDL): The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength.

3.14 Instrument Performance Check (IPC): A specific test to evaluate the performance of the instrument.

3.15 Interference: An enhancement or depression of the atomic absorption signal of an analyte in a sample when compared with an aqueous standard of the same concentration.

3.16 Laboratory Fortified Blank (LFB)=Laboratory Control Sample (LCS): A regent water blank to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.17 Laboratory Duplicates (DUP): Two aliquot of the same sample taken in the laboratory and analyzed separately with identical procedures. The DUP indicates

precision associated with laboratory procedures, but not with samples collection, preservation, or storage procedures.

3.18 Laboratory Fortified Sample Matrix (LFM)=Matrix Spike (MS): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes positive or negative bias to the analytical results.

3.19 Laboratory Fortified Sample Matrix Duplicate (LFM)=Matrix Spike Dup (MSD): Two aliquot of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of MS and MSD indicates precision associated with laboratory procedure.

3.20 Laboratory Reagent (Method) Blank (LRB): A reagent water blank carried through the entire analytical sample preparation procedure and is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and apparatus. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the regents, or the apparatus.

3.21 Linear Range: The concentration range over which the analytical curve remains linear. Determined in the initial method development and performance demonstration.

3.22 Method Detection Limit (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from an analysis of a sample in a given matrix containing the analyte.

3.23 Peak area: The area under a peak, designated as A-s.

3.24 Peak Height: The highest absorbance signal of an absorbance peak profile.

3.25 Peak Profile: The absorbance vs. time signal.

3.26 Prefill Step: The first step in a FIAS program. It ensures that all the tubes are filled with the correct solutions.

3.27 Precision: A measure of the degree of agreement among replicate analyses of a single sample or duplicate usually expressed as the standard deviation or % difference.

3.28 Proficiency Evaluation Samples (PE): EPA water studies and in house quality control using secondary reference materials provided by QA Manger. The purpose of PE sample is to evaluate the laboratory performance and analyst performance.

3.29 Quality Assurance: A definite plan for laboratory operation that specifies the measures used to produce data of known precision.

3.30 Quality Control: Set of measures within a sample analysis methodology to assure that the process is in control.

3.31 Sensitivity: Characteristic mass for the techniques that produce peak-shaped signals.

3.32 Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using standards purchased from a commercial source.

3.33 Replicate: Repeated operation occurring within an analytical procedure. Minimum of three data points for each method of analysis is required.

4.0 INTERFERENCES

4.1 Interferences have been reported for waters containing sulfide, chloride, copper and tellurium. Organic compounds which have broad band UV absorbance (around 253.7 nm) are confirmed interferences.

4.2 Volatile materials (e.g. chlorine) which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the sample container after the addition of Hydroxylamine hydrochloride should be allowed to degas for approximately 2-3 minutes (Section 9.5.4) prior to transferring into sample tubes.

5.0 SAFETY

5.1 Proper operation, maintenance, and use of laboratory facilities and safety equipment will follow the Chemical Hygiene Policy (CHP) to achieve safe working conditions. Several sections of the CHP will be reviewed prior to analysis. Such include Section 3.0 Laboratory Facilities and Section 4.0 Components of the CHP.

In addition, the following precautions should be strictly observed:

5.2 At the end of analysis, purge the FIMS Analysis System with deionized water to remove any reductant residues.

5.3 The instrument will operate correctly under the following conditions:

- temperature +15C to +35C;
- relative humidity 75% max.

5.4 Continuous ventilation must be provided for the fumes emitted from the FIMS-cell and for any other toxic products, metal vapor, and ozone that may be produced during instrument operation.

5.5 Special precautions should taken in the safe use and handling of cryogenic liquids (See Attachment 5.1). All rules and regulations of CHP apply.

5.6 MSDS sheets of all standards and reagents are provided in the metals laboratory office. Before analysis or preparation of reagents the MSDS sheets should be read and understood by all analysts.

5.7 Good housekeeping is strongly enforced. Safety glasses, lab coats and gloves will be used at all times during preparation and analysis of samples. Work areas will be left clean, samples will be properly disposed of, and reagents/standards will be stored in proper containers.

5.8 Employees will attend weekly safety and QA meetings.

6.0 APPARATUS & EQUIPMENT

6.1 The FIMS Spectrometer:
The FIMS spectrometer consists of an atomic absorption spectrometer specifically designed to measure the absorption of mercury and a flow injection system to prepare the samples for the spectrometer.

A. Software:
AA WinLab is the name of the software application.
AA WinLab uses a graphics user interface running under Microsoft Windows.

B. Components of the Front Panel of FIMS:
See Figure 6.1

C. Components on the Rear Panel of FIMS:
See Figure 6.2

6.2 The Optical Unit:
The optical unit is in the upper part of FIMS. It contains the radiation source (Hg Lamp), the FIMS-cell compartment and the photocell detector.

A. Radiation Source:
The radiation source (line source) is a low pressure mercury lamp.

B. Detector:
The detector is a photocell with maximum sensitivity at 254 nm.

C. FIMS-Cell:
The mercury vapor flows into the FIMS-cell where the absorption of the mercury is measured. The FIMS-cell has an inner diameter of 4 mm and an optical pathlength of 260 mm. The cell is heated to about 50EC to prevent the formation of condensation.

6.3 Flow System Components:

A. Pumps:
FIMS uses peristaltic pumps to transport the various liquids through the system. The speed of the pumps is under software control: 20-120 rpm or off. See Figure

B. Magazines:
Each pump accepts up to four magazines which hold the pump tubes. There are different magazines for the different sizes of pump tube. The pressure adjustment lever regulates the pressure applied to the pump tubes.

C. Pump Tubes:
A variety of pump tubes with differing diameters are available. The different sizes have different colored collars.

D. Flow-Injection Valve (FIAS-Valve):
Five-port flow injection valve with two positions, **Fill** and **Inject**.
In the **Fill** position the sample is drawn into the sample loop. The carrier stream flows continuously to the manifold.
In the **Inject** Position the sample loop is switched into the carrier stream and the sample is transported to the manifold. The sample pump is stopped while the valve is in the Inject position. For normal flow-injection analyses, port 1 is closed with a screw plug. See Figure 6.4.

E. Sample Loops:
The sample loops are made from PTEE tube and have screw connectors. The sample loops are available in different lengths with volumes between 50 uL and 1000 uL.

F. Carrier Gas System:
An inert carrier gas is required for mercury determinations with FIMS. The carrier gas carries the mercury vapor form the manifold to the FIMS-cell in the spectrometer unit.

The inlet for the carrier gas is on the rear of FIMS (the **GAS IN** connection). FIMS has a gas economy function: When FIMS is not used for more than 10 minutes the gas flow is automatically turned off.
The gas outlet, flow regulator and flow gauge are on the front panel of FIMS. The gauge is calibrated for argon. Useable flows are between 40mL/min and 250mL/min at a recommended gas inlet pressure between 320 kPa and 400kPa. The gas flow is off (0 mL/min) when the control knob is turned fully clockwise.

G. Nonreturn Valve:
The nonreturn valve at the gas outlet prevents liquid from the manifold entering the gas control system.

H. Manifold:
In the manifold two fluid streams are mixed. This can be to initiate a reaction or to dilute one of the streams. The manifold blocks have three channels that are interconnected, one channel for incoming carrier, one for incoming reagent, and the last for outgoing mix.

I. Gas/Liquid Separator:
The gas/liquid separator is used in the mercury cold vapor technique to separate the gas and liquid in the mixture that leaves the manifold.

7.0 REAGENTS & STANDARDS

7.1 1% Nitric Acid (HNO3):
Use 1% nitric acid for preparing all reagents, calibration blanks, calibration standards and as dilution water. Record date prepared, lot number, and analyst in Nitric Acid Logbook.

7.2 3% HCl (Carrier Solution):
Prepare using 30 mL conc. HCl to 1000 mL DI H2O. Record date prepared, source/lot number, and analyst in Mercury Standards and Reagents Logbook.

7.3 Mercury 1ppm Stock Standard:
Prepare a 1ppm stock standard to prepare a 0.25ppb working standard. Stock standard expiration date is three days from prep date. Follow method procedures in Mercury Laboratory Standards and Reagents Logbook, record date prepared, lot number, analyst, expiration date, and reference # in logbook.

10ppm (PEN930-0233): 10mL → 100mL 1% HNO3

7.4 Mercury Working Standards:
Prepare a series of standard mercury solutions containing the following

S1-0.25ppb (1ppm Stock Standard) → 50uL → 200mL 1% HNO3
S2-5ppb (PEN930-0233) → 50uL → 100mL 1% HNO3
S3-10ppb (PEN930-0233)→ 100uL → 100mL 1% HNO3

Working standards expiration date is three days from prep date. Follow method

procedures in Mercury Laboratory Standards and Reagents Logbook, record date prepared, lot number, analyst, expiration date, and reference # in logbook.

7.5 Initial Calibration Verification Standard (ICVS):
Prepare a ICVS sample mid-range of calibration curve, using a different lot number or second source standard. Use ~~PerkinElmer~~ **PerkinElmer PEN930-0211 or RICA 4801-4** follow all method procedures, record date prepared, lot number, analyst, expiration date and reference # in the Mercury Standards and Reagent Logbook. Must be prepared daily.

7.6 Nitric Acid, HNO3 conc:
A matrix HNO3 sample will be prepared and analyzed for every new lot of HNO3 received. (See section 8.0 Quality Assurance)

7.7 Sulfuric acid, H2SO4 conc

7.8 Potassium Permanganate solution (KMnO4):
Dissolve 50g KMnO4 in 1% HNO3 and dilute to 1 liter. Record in Standards Book.

7.9 Potassium Persulfate solution (K2S2O8):
Dissolve 50g K2S2O8 in 1% HNO3 and dilute to 1 liter. Record in Standards Book.

7.10 Sodium Chloride-Hydroxylamine Hydrochloride solution (NaCl-NH2OH*HCl):
Dissolve 120g NaCl + 120g (NH2OH)2*HCl in 1% HNO3 and dilute to 1 liter. Record in Standards book.

7.11 Stannous Chloride solution (SnCl2):
Dissolve 13.2g SnCl2 + 30 ml conc. HCl and dilute to 1000 ml DI H20. Prepare daily and record in Standards Book.

8.0 QUALITY ASSURANCE/QUALITY CONTROL

8.1 QUALITY ASSURANCE:

A set of operating principles that, if strictly followed during sample collection and analysis, will produce data of known and defensible quality. That is, the accuracy of the analytical result can be stated with a high level of confidence.

8.1.1 Chemicals/Reagents/Gases:

Ultra Pure chemicals and Ultra High Purity gases or better will be used for all metals analyses. Standards will be supplied with a Certificate of Analysis showing Manufacturer's number, Description, Lot number, Expiration date, Labeled and Measured values and Traceability to NIST SRM's. Individual analytical approved methods may specify additional requirements for the reagents to be used. All reagents will be logged and dated as to the date received and date opened with the analyst's initials, follow all SOP's for chemical receiving. No chemical/reagent will be used past its expiration date. All expired reagents will be disposed of in the proper manner.

8.1.2 Contamination:

The following precautions contribute to avoiding inorganic contaminants.

General and customary **safety practices as well as those included in instrument manufacturer's manuals and approved methods will be strictly followed. Material Safety Data Sheets will be consulted before using any new or unknown chemical/reagent.

****Glassware preparation**: All glassware used for metals analyses will be separate from all other in the Lab and be specified as such. Only Class A volumetric glassware will be used. All glassware will be cleaned according to the following procedure:

Between sample transfers:
1) Rinse with 1:1 nitric acid
2) Rinse with RO/DI water
3) Rinse with sample

After use:
1) Wash with detergent (Alconox or Contrad), by hand or in pipet washer.

2) Rinse with tap water
3) Rinse with 1:1 nitric acid
4) Rinse with RO/DI water 2X
5) Place in rack and cover

8.1.3 HNO3 Testing:

Analysis of a HNO3 blank will be analyzed with every new lot of HNO3 prior to usage. This will eliminate any possible contamination of HNO3. Record in the HNO3 Logbook.

8.1.4 Containers:

Falcon 4020 Specimen Container are to be used for containment of mercury samples. These containers have proven to be Hg free and no other container will be used.

8.1.5 Method Development Study (Internal Quality Control):

Before any analytical method is routinely employed, a methods development study will be undertaken to insure compliance with all published criteria. The instrument manufacturer's methods manuals and the selected analytical method source are excellent reference materials.

A.) Sensitivity checked (ABS-vs-CONC..) with mfr's published values +/- 10%.
B.) Linearity check of the concentration range of interest using 3 standards and a blank with a minimum of 3 replicate readings with the mean and standard deviation of the absorbance value calculated. Plot absorbance vs. concentration and calculate the correlation coefficient. The value should be 0.995 or better. If not, correct and repeat.
C.) Detection limits computed for each analyte according to Appendix B to Part 136,40 CFR, Revision 1.11.
D.) Accuracy checked with Certified known concentrations.
E.) Precision checked with duplicates or replicate analyses.
F.) Sample matrix interferences checked with spikes on all new matrices.
Recoveries should be within those limits specified in 18th Edition Standard Methods for that analytical method (85-115%).

8.1.6 Method Detection Limit (MDL):

MDL=s must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water

and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

MDL = (t) x (S)
where: t = students= t value for a 99% confidence level and a standard deviation estimate with n-l degrees of freedom {t=3.14 for seven replicates].
S = Standard deviation of the replicate analyses.
Note: If additional confirmation is desired, reanalyze the seven replicate aliquots on two or more nonconsecutive days and again calculate the MDL values for each day. An average of the three MDL values for each analyte may provide for a more appropriate MDL estimate. See Attachment 8.1

MDLs will be determined **ANNUALLY**, when a new operator begins work or whenever, in the judgement of the analyst, confirmed by the supervisor, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be re-determined.

8.1.7 Analyst Training:
All analysts will be under strict supervision for the first 6 months upon learning a new instrument procedure. A training class will be provided (usually done by Perkin Elmer), at the end of the 6 month training period a in-house PE sample will be issued to the analyst. Also a written exam in reference to operating procedures and chemical hygiene policies will be issued, upon completion of exam and PE the analyst will perform the duties required with limited supervision. See section 13 for complete training program. Training requirements will also apply for analysts on rotation schedules. Refer to QA Manual Section 14.

8.1.8 Mercury Laboratory Standards and Regents Logbook:
All reagents and standards will be recorded in the Mercury Standards Log. The standard book will provide a method for preparation of standards which will include the stock standard and vendor, the amount of mls that will be used, and the total volume that will be prepared (CIVI=CFVF).

The analysts will record the **DATE PREP**, **ANALYST INITIALS**, **LOT NO.**, **EXPIRATION DATE**, and **REFERENCE NO** in the Logbook. The reference number will correspond to the page of the specific standard-date analyzed (For example 22-031598, 22 is the page of number 031598 is the date prepared). The reference number, expiration date and analyst initials will be added to the container of the

specific standard.

8.1.9 Corrective Action Logbook:

Each instrument will be provided with a logbook for recording all corrective actions that take place with instrument control and/or sample analysis. Samples that do not meet the acceptable criteria will also be texted, using standard language, in SQLLIMS. The log book will also be used to document any problems that may occur prior to analysis. The purpose of this logbook is to monitor trends in instrument and sample analysis.

8.1.10 Equipment Preventive Maintenance Procedure:

There are two sections to the Maintenance and Repair Logbook, section one is the Maintenance Log which will be the responsibility of the analyst, running the instrument in question, to perform the specified duties on a daily routine. A Instrument Maintenance Log Book will be maintained by the Spectroscopy Supervisor. This logbook will include all service reports generated by Perkin-Elmer. It will be the responsibility of the supervisor to order the service reports from Norwalk.

8.1.11 Performance Audits:

EPA PE and in-house PE samples will be provided to the metals quarterly by the QA Manager. Two Water Pollution Studies (WP) and two Water Supplies Studies(WS) will be performed by all analysts known to be trained and proficient in the procedure involved. Performance of EPA samples will be evaluated and reported by the suppler of the proficiency samples. All in-house proficiency samples will be evaluated by WQL Quality Manager. See QA Manual Section 15.

8.1.12 Internal Quality Audits:

The Quality Manager at WQL will conduct internal quality audits of the analytical procedures being performed by the staff. The internal quality audit will include observation of standard operating procedures, evaluation of the procedure for adequacy and precision, and evaluation of correct safety procedures. Proficiency samples are frequently submitted as a part of the audit process. Internal audits will be conducted yearly for all active SOPs. See QA Manual Section 8.

8.1.13 Prioritization of Sample Type:

Due to the diversity of samples, the metals lab will employ a priority plan to run sample types in the following order Water, Environmental Health, Urban Waters, Pretreatment, and Sludge. These procedure will help to eliminate cross contamination. RULE: RUN THE CLEANEST SAMPLE TO THE DIRTIEST.

8.1.14 Data Assessment Procedure for bias and precision:

A. Laboratory Performance:

- **LRB**-data is used to assess contamination from the laboratory environment. LRB values that exceed the MDL indicate laboratory or reagent contamination should be suspected. When LRB values constitute 10% or more of the analyte level determined for a sample or is 2.2 times the analyte MDL whichever is greater, fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.

< **LCS**-Calculate accuracy as percent recovery using the following equation:

$$R = \frac{LCS-LRB}{s} \times 100$$

R =percent recovery
LCS=Laboratory Control Sample/Laboratory Fortified Blank
LRB=Laboratory Reagent (Method) Blk
s =concentration equivalent of analyte added to fortify the LRB solution

The laboratory must use LCS analyses data to assess laboratory performance against the required control limits of 85-115%. If the recovery of any analyte falls outside the required control limits of 85-115%, that analyte is judge out of control, and the source of the problem should be identified and resolved before continuing analyses.

When sufficient internal performance data become available (usually a minimum of twenty to thirty analyses), optional control limits can be developed from the mean percent recovery (x) and the standard deviation (S) of the mean percent recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x + 3S

The control limits must be equal to or better than the required control limits of 85-115%. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent twenty to thirty data points. Also, the standard deviation (S) data should be used to established an on-going precision statement for the level of concentrations included in the LCS. These data must be kept on file and be available for review.

< **ICVS:** When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a second source standard (ICVS). If the determined concentrations are not within +/-10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before continuing with on-going analyses.

< **CCVS**: The laboratory must analyze the CCVS after every tenth sample and at the end of the sample run. Subsequent analyses of the CCVS must be within +/-10% of the calibration. If the calibration cannot be verified within specific limits, reanalyze either or both the CCVS and the calibration blank. If the second analysis of the CCVS or calibration blank confirm the calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift the instrument recalibrated. ALL SAMPLES FOLLOWING THE LAST ACCEPTABLE CCVS SOLUTION MUST BE REANALYZED.

B. Assessing Analyte Recovery and Data Quality:

< **MS/MSD:** Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess these effects. The analyte interference effects are operative in selected samples.

The laboratory must run a MS&MSD for every batch. In each case the MS aliquot must be a duplicate of the aliquot used for sample analysis and for total recoverable determination added prior to sample preparation. The added analyte concentration must be the same as that used in the laboratory fortified blank. Over time, samples from all routine sample source should be fortified.

Calculate the percent recovery for each Hg analyte, corrected for concentration measured in the unfortified sample, and compare these values to the designated MS recovery range of 70-130%. RECOVERY CALCULATIONS ARE NOT REQUIRED IF THE CONCENTRATION ADDED IS LESS THAN 25% OF THE UNFORTIFIED SAMPLE CONCENTRATION. Percent recovery may be calculated using the following equation:

$$R = \frac{Cs - C}{s} \times 100$$

R = percent recovery
Cs= fortified sample concentration
C = concentration equivalent of analyte
s = concentration equivalent of analyte added to fortify the sample

If the recovery of any analyte falls outside the designated MS recovery range (but is still within the range of calibration) and the laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the MS is judged to either matrix or solution related, not system related. All actions will be recorded in Corrective Action Logbook and the sample will be texted in LIMS as possible matrix interference.

8.1.15 Sample Control and Documentation:

A. Control Charts:
Two control charts will be generated for each analyte per instrument.

MEASURE ACCURACY CONTROL CHART 1:
Percent Recovery= LCS-LRB/s x100

MEASURE PRECISION CONTROL CHART 2:
Percent Difference= [LCS-LCSD]2/LCS+LCSD X100

Note: All quality control data will be documented and files will be keep in the Control Data Logbook.

B. Corrective Actions:
All corrective actions will be documented in the Corrective Action Logbook.

8.1.16 Data Reduction/Reporting/Validation:

A. Data Reduction:

< **Instrument Criteria**: All instrument control data will be reported +/- percent difference from expected values. This will include ICVS and CCVS values.

Calculation: $\frac{\text{Value Read - Expected Value}}{\text{Expected Value}} \times 100$

Note: Reports will read + or - of Expected Value

< **Sample Criteria:** All sample control data will be reported as percent difference or percent recovery of absolute value.

LCS	Calculation: $\frac{\text{LCS-LRB}}{\text{s}} \times 10$	%Recovery
LCSD	Calculation: $\frac{[\text{LCS-LCSD}]2}{\text{LCS+LCSD}} \times 100$	%Difference
MS	Calculation: $\frac{\text{Cs-C}}{\text{s}} \times 100$	%Recovery
MSD	Calculation: $\frac{[\text{MS MSD}]2}{\text{MS+MSD}} \times 100$	%Difference

Note: MSD %Difference must be absolute value of 10% or better.
LCS %Recovery within 85-115%
MS %Recovery within 70-130%
***Control Chart LCS and LCSD

B. Reporting:

All laboratory data is entered via SQLLIMS system. Laboratory analysts are responsible for the data and result entry of the data produced daily. All data entries will be performed at the TASK LEVEL ONLY. See QA Manual Section 4.

When available the result entry using ARE will be used for instrument generated data. When this system is not available manual data entry will be used.

C. Validation: Result approval is performed at the TASK level only. A second analyst

other than the analyst entering the data will verify and approve all data entry. Two signatures will be signed on all reports, the first will be the signature of the analyst who performed the test and enter the data. The second signature will be initialed by a second analyst who will validate the first analysts data.

Out of Spec Data:
A third validation will be initialed by the supervisor if QA/QC limits are out of spec. If the QA/QC requirements are not within reporting limits; data will be reviewed by supervisor. At this time samples may be re-prepped or corrective actioned. This process is to insure proper sample prep, proper entry and calculations of all data in the metals lab.

Changes In Data: Changes in data will be performed at the TASK level only. All changes in LIMS must be approved by supervisor.

8.2 Quality Control:

8.2.1 Quality Control Requirements:

The minimum requirements of this QC program consist of an initial demonstration of laboratory capability, and periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

***Calibration**

*Calibration Curve - Blank & 3 Standards
*Calibration Verification - Blank & Standard

***Sample Analysis**

*Laboratory Reagent Blank - < MDL
*Laboratory Fortified Blank - Minimum one per batch
*Laboratory Fortified Sample Matrix - Minimum one per batch
*Laboratory Fortified Matrix Duplicate Sample - Minimum one per batch

***Periodic Requirements**

*EPA PE Samples - Quarterly
*Method Detection Limit - Annually

*In-house PE Samples - Quarterly

8.2.2 Instrument Performance:

Determination of linear dynamic ranges and analysis of quality control samples.

***Calibration Blank (Cal Blk)**

*Acid Blank Matrix
*Auto -zero instrument
*Control Limits - Ongoing Analysis < MDL
*Frequency - Before calibration, prior to sample analysis and after every CCVS
*Corrective Action - If > MDL terminate run and correct before proceeding
*Check - 1% HNO3 contamination
*Record - Corrective actions in logbook

***Initial Calibration Standards (ICAL)**

*Minimum of 3 pt calibration S1/S2/S3
* Ist source vendor - Perkin Elmer
*Control Limits - Correlation coefficient equal or greater than 0.995 for curve
*Frequency - Prior to analysis of each analyte and if CCVS criteria not meet
*Corrective Action - If criteria not meet recalibrate
*Check -Expiration date of standards, methodology applied and calculations
*Record - Corrective actions in logbook

***Initial Calibration Verification Standard (ICVS)**

*Mid-range of calibration curve
*2nd source vendor - JT Baker
*Control Limits - +/- 10% expected value
*Frequency - One per each calibration curve produced
*Corrective Action - If criteria not meet rerun 2nd time, if still not corrected recalibrate
*Check -Expiration date of standard, methodology applied and calculations
*Control Chart - Verification of instrument control done for each analyte
*Record - Corrective actions in logbook

***Continuing Calibration Verification Standard (CCVS)**

*Mid-range ICAL = S2
*Control Limits - Ongoing +/- 10% stated value
*Frequency - Every 10th sample and end of run

*Corrective Action - If criteria not meet rerun 2nd time, if still not corrected recal and all samples following the last acceptable CCVS must be reanalyzed
*Check - Expiration date of standard, methodology applied and calculations
*Record - Corrective actions in logbook

8.2.3 Laboratory Performance:

Determination of method detection limits.

***Laboratory Reagent (Method) Blank (LRB)**

*reagent water
*Control Limits - Analyze conc < MDL
*Frequency - Each batch of 20 or fewer samples
*Corrective Action - When LRB values constitute 10% or more of the analyte level determination for a sample or is 2.2 times the analyte MDL whichever is greater, fresh aliquot of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.
*Check - Laboratory or reagent contamination should be suspected
*Record - Corrective actions in logbook

***Laboratory Control Sample (LCS)**

*Control Limits - Recovery 85-115%
*Frequency - One LCS per batch
*Corrective Action - Source of the problem should be identified
*Check - Source of the problem should be identified & resolved before continuing
*Record - Corrective Actions must be recorded in laboratory logbook
*Control Chart -Verification of laboratory performance done for each analyte
*Record - Corrective actions in logbook

***Laboratory Control Sample Duplication (LCSD)**

*Analyte concentration must be the same as that used in the LCS
*Spiked sample will be carried through same analytical procedures as LCS
*Control Limits - Percent difference of +/-10% between LCS & LCSD
*Frequency - One per batch of 20 samples or less
*Corrective Action - Source of the problem should be identified & resolved
*Check - Spike solution and sample prep technique
*Record - Corrective actions in logbook

8.2.4 Data Verification:

Defines the quality of data generated.

***Laboratory Fortified Matrix (MS)

*Analyte concentration must be the same as that used in the LFB

*Spiked sample will be carried through the same analytical procedure as samples

*Control Limits - Percent recovery for each analyte of 85-115%

*Frequency - One per batch

*Corrective Action - Source of the problem should be identified & resolved

*Check - Spike solution, methodology applied and sample prep technique

*Caution - Addition of a volume of spiking solution grater than 1-2% of the sample volume may result in significant dilution error. If the volume of the spiking solution is within 2% of the sample volume, correction for dilution is not needed.

*Record - Corrective actions in logbook

***Laboratory Fortified Matrix Duplicate (MSD)

*Analyte concentration must be the same as that used in the LFB

*Spiked sample will be carried through same analytical procedures as MS

*Control Limits - Percent difference of +/-10% between MS & MSD

*Frequency - One per batch of 20 samples or less

*Corrective Action - Source of the problem should be identified & resolved

*Check - Spike solution and sample prep technique

*Record - Corrective actions in logbook

***Field Duplicates

*At discretion of sampling organization

***Field Blanks

*A field blank should be prepared and analyzed as required by the data user. *Use the same container and acid as used in sample collection.

9.0 PROCEDURE

9.1 General:

Before operating the instrument for the first time, it is required that the analyst familiarize him- or herself with the operating controls and other aspects of the analysis.
Standard Operating Procedure (SOP) and the FIMS Installation Maintenance System Description Manual should be reviewed. In-house proficiency will be mandated of all analysts performing analyses.

9.2 Sample Handling:

A. Collection:

All samples received and handled by this section will meet the requirements of the Policy and Procedure Manual of the Water Quality Lab pertaining to handling and preservation criteria.

Samples will be logged by the Sample Custodian and assigned a unique log number. Pertinent information, i.e. location, date and time of collection, collector's name, sample type, date received by this section, person's name receiving the sample, preservation used, and any special remarks concerning the sample will be entered into the computer.

A batch number will be assigned by this section. All batches will be numbered with reference to protocol and year, for example pretreatment batches will be assigned PRE9801 beginning with 01 for batch one of the 98 year.

B. Preservation and Preparation:

All mercury samples will be prepared following Standard Operating Procedures Sample Preparation Manual. Samples will be preserved with the addition of 2.5 ml HNO3 and 5 ml H2SO4 in sample container appropriate for mercury.

C. Storage:

Samples that may have legal ramifications due to not being within regulatory compliance limits are to be stored in a secure area but for no longer than their allowed holding times. Confer with the supervisor before discarding any samples.

D. Holding time:

All samples will be stored in the spectroscopy refrigerator in the sample preparation area until analysis. Analysis will be performed within 28 days of sample date.

9.3 Preliminary preparations:

9.3.1 Prepare hot water bath apparatus. Temperature should be 95C, record in the Sample Prep Book.

9.3.2 Prepare SnCl2 reductant solution & 3% Hcl carrier solution. Record in Standards Prep Book.

9.3.3 Prepare standards, QA samples, and calibration blanks. (As specified in section 7.0) Record in Standards Prep Book.

9.3.4 KMnO4, K2S2O8, and hydroxylamine reagents may be prepared the day prior to analysis. Record in Standards Prep Book.

9.3.5 Fill all dispenser containers with the appropriate reagent. Set dispensers to dispense as follows:
K2S2O8: 8ml
KMnO4: 15ml
Hydroxylamine: 6ml

9.3.6 Add K2S208 + KMnO4 to all samples, standards, and blanks and digest for two hours at 95 C. Allow samples to cool, add Hydroxylamine; mixing sample to dissolve all K2S2O8. Transfer to 15 ml tubes.

9.4 Starting Up the System:

9.4.1 Before you use FIMS, make sure that:

< The FIMS-cell and the tubing are correctly installed.
< The waste vessel is empty and the waste tubes lead to the waste vessel.
< The pump tubes are not worn.
< Make sure that the DIP switch settings (communication interface and parameters) on the rear of FIMS correspond with the entries in the HARDWARE.INI file.

9.4.2 Switching On the System:

Switch on the various parts of the system in the correct order:

1. Turn on the carrier gas supply and adjust the pressure to 3.6 bar (52 psig)
2. Switch on FIMS.

The power switch for FIMS is at the left-hand side of the front panel.

< When you press the power switch to the **ON** position, the green control light under the switch illuminates. The instrument is ready for use. The FIMS-cell heating and the source lamp are switched on automatically when the power is on.

< When you press the power switch to the **OFF** position, the green control light under the switch goes out and **O** is shown on the upper edge of the switch. All instrument functions are interrupted.

3. Switch on the computer and printer and start Windows.
4. In the Program Manager, double click on FIMS and then double click on the **AA WinLab** icon.

Note: AA WinLab appears and it takes a short time for the system to run through the initialization procedure. When the initial screen appears you can proceed.

On the initial screen there are Laboratory Procedure icons which represent window layouts. Click on an icon to open the layout. You can make your own layouts with the **Save As----Lab. Procedure** command in the File menu.

To remove the initial screen, click on **Menus and Toolbar**.

9.4.3 Recommended Tubing Configuration:

See Figure 9.1.

9.5 Starting and Adjusting the Flows:

1. Make sure that the tubing configuration is set up correctly.
2. Disconnect the sample transfer tube joining the gas/liquid separator to the FIMS-cell, at the FIMS-cell.

Place the Free end of the sample transfer tube in a beaker to collect any liquid that enters the tube.

Note: This prevents liquid entering the FIMS-cell if the liquid in the gas/liquid separator overflows. If liquid enters the fims-cell, clean the cell as described in Maintenance section.

3. Set the carrier gas flow to the value suggested in the Recommended Conditions window. Use the gas flow regulator and the flow gauge on the front of FIMS.

Note: If there is no gas flow, the automatic gas valve may be closed. To start the flow,in the **FIAS Control** *window, click on* **Valve Fill/Inject**.

Turn of and adjust the carrier gas flow before you start the pumps. This

prevents liquid entering the nonreturn valve, clean the valve as described in the Maintenance section.

9.5.1 Starting the Pumps:

1. Place the inlets of the carrier pump tube (yellow/blue), reductant pump tube (red/red) and sampling tube (leading to the FIAS-valve) in containers of deionized water.
2. Swing the pump pressure levers over to press the pump tube magazines against the rollers.
3. On the **Toolbar**, click on **FIAS**.
   Then, in the **FIAS Control** window:
   a) Click on **Valve Fill/Inject** to set the valve to the **Fill** position.
   b) Type **100** for **Pump #1 Speed**.
   c) Click on **PUMP #1**
4. Make sure that there are no leaks.
5. Adjust the Pump Pressure
   Adjust the pressure on the pump tubes with the screws on the pressure levers. Apply as little pressure as is necessary to give a smooth flow without bubbles.
   Note: To avoid unnecessary wear or erratic flow, do not use very high or low pressure on the tubes. Too much pressure on the pump tubes ruin them.

9.5.2 Setting the Carrier and Reductant Flows:

Adjust the carrier and reductant flows to give a carrier flow between 9 -11 mL/minute and a reductant flow approximately one half of the carrier flow-between 5-7 mL/minute.

A. Measuring the Carrier Flow:

1. Make sure that there are no blockages, leaks or damaged tubes.
2. Fill a graduated cylinder with deionized water.
3. Place the carrier tube inlet in the graduated cylinder.
4. After one minute note the decrease in volume. The flow should be between 9 and 11 mL/minute.
5. If the carrier flow is not within this range, adjust the pressure on the carrier pump tube until the flow is within this range.

B. Measuring the Reductant Flow:

1. Fill a graduated cylinder with deionized water.
2. Place the reductant tube inlet in the graduated cylinder.
3. After one minute note the decrease in volume. The flow should be

approximately one half of the carrier flow - between 5 and 7 mL/minute.

4. If the reductant flow is not within this range, adjust the pressure on the reductant pump tube until the flow is within this range.

9.5.3 Setting the Gas/Liquid Separator Outflow:

1. Place the inlets of the carrier and reductant pump tubes into a container of deionized water.
2. Make sure that the sample transfer tube joining the gas/liquid separator sample outlet to the FIMS-cell is disconnected at the FIMS-cell.

   Place the free end of the sample transfer tube in a beaker to collect any fluid that may enter the tube.
3. Alter the pressure on the waste pump tube to adjust the rate at which liquid leaves the gas/liquid separator. Increase the pressure on the pump tube until bubbles appear in the waste outlet tube of the gas/liquid separator.

   Note: The rate at which liquid leaves the gas/liquid separator should be slightly greater than the rate at which it enters.
4. Make sure that the sample transfer tube is clean and dry. Reconnect the sample transfer tube from the sample outlet of the gas/liquid separator to the FIMS-cell.
5. Turn off the pumps:

   In the **FIAS Control** window, click on **Pump #1.**

9.6 Optimization

Optimize the signal each time you start a new analysis and whenever you alter the fluid system in any way.

9.6.1 Preparation:

1. Set up the tubing and adjust the flows as described in section 9.4.

   Make sure that the sample transfer tube is connected to the FIMS-cell.
2. Prepare a blank solution, the recommended carrier and reductant solutions, and the recommended sensitivity-check solution. See the Recommended Conditions window (from the **Tools** menu, choose **Recommended Conditions**).
3. On the **Toolbar**, click on **MethEd**. Open either the default method or create a custom method.

   Use the **Method Editor** to set the following parameter values:

< On the **INST** page, set the **Read Delay** valve to zero.

< On the **INST** page, set the **Read Time** value to 15 seconds.

< On the **Calib** page, enter **10** for **Replicates.**

Close the **Method Editor**.

4. From the **Toolbar** or **Tools** menu, open the **Display Peaks**, **FIAS Control** and **Manual Control** windows or go into AWKSPACE≅ icon.
5. Before you make measurements, allow the lamp to warm up for 30 to 45 minutes.
6. Swing the pump pressure levers over to press the pump tubes against the pump rollers.
7. Place the carrier tube (yellow/blue) inlet in the carrier solution, and the reductant tube (red/red) inlet in the reductant solution.

9.6.2 Making Measurements and Adjustments:

A. Measure the Blank Solution and Perform an Autozero:

1. Place the sampling tube inlet in the blank solution.
2. On the **Toolbar**, click on **Manual**.
3. In the **Manual Analysis Control** window, click on **Analyze Blank**.
   To stop the analysis for any reason, click on **Analyze Blank** *again.*

B. Measure the Reference Solution:

1. Place the sampling tube inlet in the reference solution.
2. In the **Manual Analysis Control** window, click on **Analyze Sample**.
   or...In the **FIAS Control** window, click on **FIAS On/Off**.
   The signal for the first replicate appears in the **Display Peaks** window.
   ******500uL of a 10ug/L solution = 0.1A******

C. Optimize the Signal:

< If necessary, make adjustments as suggested below. After each adjustment wait until the next signal appears before you make a further adjustment.
< Alter only one parameter at a time.
< If all the replicates have been run before you have finished, click on **Analyze Sample** or **FIAS On/Off** to start the program again.
< When you have finished, calculate the characteristic mass as described below.
< If you do not wish to make measurements immediately, release the pressure on the pump tubes.

D. Procedures for Optimizing the Signal:

! The absorbance values for each replicate should be similar. If the absorbance for the first replicate is higher than that for the subsequent ones, lengthen the **Fill** step

on the **FIAS** page of the Method. If the absorbance of the first replicate is lower, lengthen the **Prefill** step.
Ensure that the **Read Delay** (0s) and **Read Time** (15s) values are set correctly on the **Inst** page of the Method.
Slight adjustments to the gas flow may improve sensitivity. If the peak maximum appears too early, slightly decrease the carrier gas flow.
If the peak maximum appears too late, slightly increase the carrier gas flow.
Note: If the carrier gas flow is too high, the mercury vapor is dispersed too rapidly. If the flow is too low, mercury vapor flows into the cell too slowly. In both situations the signal and sensitivity are low. A flow in the range 40-70 mL/min is generally suitable.
A slight decrease in the outflow from the gas/liquid separator may improve sensitivity.
Note: If the outflow from the gas/liquid separator is too high, mercury vapor may escape through the waste outlet. If the outflow is too low, the fluid level may rise so high that moisture escapes into the sample transfer tube and the FIMS-cell. If liquid does enter the FIMS-cell, you must clean cell as described in Maintenance.

! Slight adjustments to the carrier and reductant flows may improve sensitivity.
! If the FIMS-cell is contaminated, clean the cell as described in Maintenance section.

9.7 Sample Analysis

9.7.1 Entering Information in the Automated Analysis Control Window:

< On the **Toolbar**, click on **Auto**.
< Select the correct **Method**:
Double click on the **Method** column.
Double click on **Method Name** that you require.
< Specify the autosampler locations of the samples to analyze: Either select the check box in the column labeled: **Sample Info. File**.
Or enter the locations in the column labeled: **Locations as listed below**. Enter individual locations or a range of locations. Use commas to separate the locations and ranges, e.g. **10-15,18,20,22, 25-30.**

If you use a Sample Information File, these locations must correspond with locations specified in this file.Do not enter locations of blanks, QC=s, checks or calibration solutions.
< Select the correct **Sample Information File**.

We recommended that you use a Sample Information file to store information about the samples. The system uses this file to label the data from your samples and to calculate final concentrations.

< Select the name of the **Results Data Set** where you will save the results.
If the data set exist, new data will be added to it.
< Select the **Save Data** check box if you want the results saved in the data set specified.
< Select the **Print Log** check box if you want the results to be printed.
< Select the **Off After Analysis: - Lamp, Pumps** check boxes to switch these items off at the end of the analysis.

9.7.2 Loading the Autosampler Tray:

< In the **Automated Analysis Control** window, select the **Analyze** tab.
< Click on **Load Tray**.
< Place the loaded sample tray in the autosampler, or load the samples and other solutions (calibration, check, reslope, wash) into the sample tray in the autosampler.
Make sure that the solutions are in the locations which you specified int eh Method and the Sample Information file.
Make sure that the tray is the same one as specified in the Method and the locations 1-8 are at the front.
< Click on **Reset...**

9.7.3 Starting the Analysis:

To analyze all the solutions:

< In the **Automated Analysis Control** window, click on **Analyze All**.
All the solutions will be analysed. The calibration solutions will be analyzed first, immediately followed by the samples and any other solutions (QC, reslope etc.).

To analyze the calibration solutions:

You can perform the calibration first, pause, then analyze the samples if the calibration is satisfactory.
< In the **Automated Analysis Control** window, click on **Calibrate**.
< When you are satisfied with the calibration, in the **Automated Analysis Control** window, click on **Analyze Samples**.
The samples and any other solutions (QC, reslope etc.) will be analyzed.

To use a previous calibration for the analysis:

Note: To use this method of performing an analysis you must be absolutely sure that the calibration is valid for the samples you wish to analyze.

On the **Toolbar**, click on **Analysis** and recall calibration.

If the calibration curve appears in the **Display Calibration** window, you may use it for your analysis.

If the calibration curve does not appear in the **Display Calibration** window, you will have to make a new calibration.

< When you are satisfied with the calibration curve, in the Automated Analysis Control window, click on Analyze Samples.

The sample and any other solutions (QC, reslope etc.) will be analyzed.

9.7.4 Performing a Recalibration:

You define the type and frequency of automatic recalibrations on the Check page of the Method.

If you need to perform an extra recalibration:

< Stop the analysis

< In the **Automated Analysis Control** window, click on **Reset...**

< In the **Automated Analysis Control** window, click on **Calibrate.**

9.7.5 Stopping the Analysis:

< If in the **Automated Analysis Control** window, click on the button you used to start the analysis **(Analyze All, Calibrate,** or **Analyze Samples).** A dialog box appears.

< In the dialog box, select one of the options, then click on **OK**. Click on **Cancel** to continue the analysis where you interrupted it.

Continuing the Analysis Where You Interrupted it or Continuing with a Specific Sample:

< In the **Automated Analysis Control** window, click on **Analyze All** or **Analyze Samples.** A dialog box appears.

< Select one of the options in the dialog box.

< Click on **OK.**

9.8 Expression of Data:

A. Data Analysis and Calculations:

9.8.1 All samples will be reported in ug/l, except for sludges and solid samples which

require units of mg/kg.

9.8.2 For dilution and concentration factors use the following equation: **See Attachment 9.1 for further dilution instructions.**

$$\text{Result} \times \frac{\text{Final Sample Volume}}{\text{Original sample Volume}}$$

EXAMPLES:
Dilution factor:
Final Sample Volume (10 ml sample + 40 ml DI/RO water) =5X
Original sample volume 10 ml

Concentration factor:
Final Sample Volume 25 ml = 0.10X
Original Sample Volume 250 ml

9.8.3 MG/KG Conversation:

$$\frac{(\text{mg/L})(\text{Final Volume ml})}{(\text{wt grams})} \times \text{Dilution Factor (2)} = \text{mg/kg}$$

or

$$\frac{(\text{ug/L})(\text{Final Volume ml})1000}{(\text{wt grams})} \times \text{Dilution Factor (2)} = \text{mg/kg}$$

B. Reporting Data:

9.8.4 Reporting MDL's- See Attachment for all current metals MDLS's. Hg's current MDL is 0.5ppb.

9.8.5 Result Approval and Verification:
The analyst running the specified tests will enter all data in the SQLLIMS. This analyst will also be responsible in acquiring a second analyst to validate the data entered. The Spectroscopy Supervisor will verify all calculations and data entries.

9.9 Shutdown Procedures:

< Rinse the sample, carrier and reagent tubing with the appropriate rinse solutions.

Use the rinse solution described in Maintenance section 10.1.3.

< Swing all the pressure levers away from the pump tube magazines.

< Empty the FIMS waste vessel and clean up any spillages. Dispose of waste solutions properly and observe safety regulations when you dispose of waste.

< Turn off the carrier gas supply at the regulator valve.

< Switch off the instrument:
Exit the AA WinLab application.
Switch off the FIMS spectrometer.
Switch off the computer and printer.

10.0 MAINTENANCE

10.1 Daily Care:
The instrument requires little maintenance other than to keep it clean. The following practices form a care routine that will maintain the instrument in good condition:

RECORD IN MERCURY MAINTENANCE AND REPAIR LOGBOOK

10.1.1 Immediately clean all spilled materials from the affected area. Take special care to clean all SnCl2 from the instrument and counter tops.

10.1.2 Argon Supply:
Make sure that an adequate supply of argon is available and connected to the system. Argon output pressure: 52 psig.

10.1.3 Fluid System Maintenance:

A. Procedure for Rinsing the Fluid System:
The procedure to use for rinsing the FIMS fluid system depends on the nature of the samples that you analyzed and the other solutions you used.

! If the sample, carrier or other reagent solutions contained organic solvents you must rinse all traces of the solvent from the FIMS fluid system. This is especially important if you intend to analyze aqueous solutions next.
! If the samples contained toxic substances you must remove all traces of these compounds from the FIMS fluid system.

1) Use 1% **HNO3** rinse solution.
2) Place the inlets of the carrier and reagent (e.g. reductant, buffer) tubes in a container of rinse solution.
3) On the **Toolbar**, click on **Auto**.
4) In the **Automated Analysis Control** window, click on **Analyze** page tab.
< Click on Select **Location....**
In the dialog box, select the **Go to wash** option, then click on **OK.**
< In the **Automated Analysis Control** window, click on **Move Probe Up/Down** to raise the sampling probe.
< Place a beaker with the rinse solution in the wash location, (usually located) see

the Calib page of the Method Editor).

< Click on **Move Probe Up/Down** to lower the probe into the rinse solution.

5) On the **Toolbar**, click on **FIAS**.

6) In the **FIAS Control** window:

< Click on **Valve Fill/Inject** to turn the valve to the **Fill** position. (The position is shown in the Status display of the window.)

7) In the **FIAS Control** window:

< Then click on the **Pump 1** to start the pumps.

8) In the **FIAS Control** window, click on **Valve Fill/Inject** a number of times while the pumps are running. This ensures that the sample channel and the inside of the FIAS-valve are rinsed effectively.

Rinse the tubing with the first rinse solution for as long as necessary to remove all traces of the previous reagent.

9) After rinsing with 1%HNO3 rinse with deionized water:

< Place the inlets of the carrier and reagent tubes in containers of deionized water.

< In the **Automated Analysis** Control window, click on **Move Probe Up/Down** to raise the sampling probe. Click on **Move/Probe Up/Down** to lower the probe into the rinse solution.

< Repeat steps 8) and 9) as necessary.

10) After rinsing with the last rinse solution (deionized water):

< Remove all the tubes from the rinse solution containers.

< Click on **Move Probe Up/Down** to rinse the sampling probe out of the last rinse solution.

< Allow the pump to run until all the tubes and the gas/liquid separator are empty.

< Click on the **Pump 1** to stop the pump.

< Make sure that the FIAS-valve is in the Fill position.

B. Pump tubes:

< To reduce wear on the pump tubes, place one drop of silicone oil on the part of the tube in contact with the pump rollers.

< Release the tension on the pump tubes when you are not using FIMS.

C. Pump rollers:

< Wipe the rollers with a dry lint free cloth.

D. All tubes:

< Daily, make sure that all the tubes are clean and free from kinks.
< Remove any tubes that may be damaged or contaminated and install new tubes

E. Waste bottle:

< Empty the waste bottle regularly; never allow it to overflow or allow the liquid to reach the end of the drain tube.
< Always follow proper waste disposal procedures (see section 12).

10.2 Semi-Annual:

10.2.1 Gas/Liquid Separator and Manifold Maintenance:

Normal Procedure:

< When you have finished an analysis, rinse the fluid system.

To clean the manifold and separator more thoroughly:

< Separate the manifold and separator blocks.
< Disconnect the tubes from the manifold and separator blocks.
< Unscrew the separator cover and remove the PTEE filter.
< Pump deionized water through each channel of the blocks.
< If necessary, use compressed air to unblock the fluid channels of the blocks.
< Rinse the manifold and separator blocks with 1:1 hydrochloric acid (one part concentrated hydocholoric acid diluted with one part water- about six molar).
< Rinse the manifold and separator components thoroughly with deionized water.

Hydrochloric acid (HCl) is corrosive and can cause severe burns. When using hydrochloric acid, always wear protective equipment.

Changing the Separator Filter:

< For successful analyses, the filter must be clean and dry.
< Unscrew the separator cover and remove the old filter.
< Insert a new filter with the smooth side down.
< Replace the cover.

10.2.2 FIAS-Valve Maintenance:

< To clean the channels of the valve individually
1) Disconnect all the tubes from the valve.
2) Pump deionized water through each channel of the valve.

If the procedure described above is not sufficient to clean the valve, you can dismantle the valve and clean the components parts as described below.

1) Disconnect all the tubes from the valve.
2) Remove the valve from the pump unit, see next section.
3) Dismantle the valve.
4) Clean the individual parts of the valve with deionized water. Pump deionized water through each channel of the valve components. If necessary, use compressed air to unblock the channels of the valve.
5) Reassemble the valve, see section below.
6) Attach the valve to the pump unit.

A. Removing the FIAS-Valve from the Pump Unit:

1) Make sure that there is no analysis in progress.
2) Disconnect all the tubes form the FIAS-valve.
3) Unscrew the two screws that secure the valve to the pump unit.
4) Gently pull the FIAS-Valve away from the motor mount.

B. Dismantling the FIAS-Valve:

1) Place the dismantling tool on the rear of the FIAS-Valve. Make sure that the lug on the dismantling tool engages the notch in the spindle. See Figure 10.1.
2) Hold the valve and dismantling tool securely and, with a 7 mm wrench, unscrew and remove the securing bolt.
3) Carefully separate the valve components. See Figure 10.2.
4) Carefully clean the valve components.

Note: Do not use metal or abrasive tools to clean the valve.

< Use deionized water or use a soft lint free cloth moistened with ethanol.
< If necessary, use compressed air to unblock the channels in the valve.
< Rinse the components thoroughly with deionized water.
< Pump deionized water through each channel of the valve components.

C. Reassembling the FIAS-Valve:

1) Check the components. If they are scratched or damaged, use new components.

Note: The valve rotor and the valve body are matched components. If either is damaged you must replace both with a matched pair of components.

2) Reassemble the valve components as seen in Figure 10.3. Make sure that the groove in the valve rotor locates correctly over the pin on the valve body.
3) Screw the securing bolt into the spindle, first by hand then use the 7 mm wrench. Do not over tighten the securing bolt.
4) Pump deionized water through the channels of the valve to make sure that the channels are open.
5) Install the valve on the pump unit.

D. ***Fitting the FIAS-Valve to the Pump Unit:***
1) Align the coupling on the spindle of the valve over the motor mount on the pump unit, then push the valve onto the motor mount.
2) Tighten the two screws that hold the FIAS-valve onto the pump unit.

10.2.3 FIMS-Cell Maintenance:

A. **Measuring the Absorbance of the FIMS-Cell Windows:**
1) Switch on the FIMS analysis system.
2) Start the AA WinLab application.
3) Open the **Continuous Graphics** window (on the toolbar, click on **Cont**).
4) Remove the FIMS-cell from the cell components of FIMS; see below.
5) In the **Continuous Graphics** window, click on **Autozero.**
6) Install the FIMS-cell in the cell compartment; see below for instructions.
7) The absorbance reading in the Continuous Graphics window is the absorbance of the FIMS-cell window.

Note: If the absorbance is greater that 0.75, remove the windows from the FIMS-cell and clean them.

B. Removing the FIMS-Cell from the Spectrometer:
1) Make sure that there is no analysis in progress.
2) Carefully disconnect exhaust tube and sample transfer tube from the FIMS-cell.
3) Grip the two nipples on the cell window assemblies and pull the cell out of the cell compartment.

C. Removing the Windows from the FIMS-Cell:
1) Pull and simultaneously twist the cell window assemblies of the ends of the FIMS-cell.

2) Carefully insert the tip of a small screwdriver in the notch of the window assembly and remove the outer O-ring. Remove the window from the cell window assembly.

D. Fitting the Windows to the FIMS-Cell:

1) Carefully place the clean windows in the cell windows assembly.
Insert the outer O-ring in the cell windows assembly to secure the window.
2) Push and simultaneously twist the cell window assemblies onto the ends of the FIMS-cell.

Note: Install the cell in the spectrometer and measure the absorption of the windows. If the absorbance is still too great, either clean the windows more thoroughly, or install new windows.

E. Cleaning The Windows:

Take care not to scratch or touch the surface of the quartz windows. You must replace windows.

The more you rub the surface of the windows, the more chance there is of scratching them. Keep cleaning solutions and water away from other parts of the instrument.

1) Remove the FIMS-cell from the cell compartment of the spectrometer.
2) Remove the windows from the FIMS-cell.
3) Wash the windows with deionized water and allow them to dry.
If the windows are not properly clean:
4) Clean the windows with a soft, lint-free cloth moistened with a spectroscopic-grade alcohol.

Note: Install the cell in the spectrometer and measure the absorption of the windows. If the absorbance is still too great, either clean the windows more

thoroughly, or install new windows.

F. Cleaning the FIMS-Cell:

1) Remove the FIMS-cell from the cell compartment of the spectrometer.
2) Remove the windows from the FIMS-cell.
3) Wash the FIMS-cell with deionized water and allow it to dry.

G. Installing the FIMS-Cell in the Spectrometer:

To install the FIMS-cell in the spectrometer, grip the two nipples on the window assemblies and carefully push the FIMS-cell into the cell compartment.

10.2.4 Changing the Air Filter:

To ensure that the components inside the spectrometer are properly cooled, the air filter must allow sufficient air into the spectrometer.
Check the filter regularly. If it is dirty, install a new one.

1) Switch off FIMS.
2) Prise up and remove the filter cover.
3) If the old filter is dirty, remove it and insert a new filter. Replacement filter, Part Number B050-2706.
4) Press the filter cover firmly back into place.

10.2.5 Carrier Gas System Maintenance:

If liquid enters the nonreturn valve, you must dismantle the valve and clean it. Periodically check the nonreturn valve. If the rubber sleeve shows signs of deterioration, fit a new one.

11.0 TROUBLESHOOTING

11.1 Problems With the Analyses:

Problem	Possible Cause	Check/Remedy
Characteristic mass too high. (Poor sensitivity)	Reductant not fresh.	Prepare fresh reductant.
	Reference solution and/or blank not fresh.	Prepare fresh solutions.
	Wrong oxidation state of element.	See the Recommended Conditions window.
	Gas/Liquid Separator Outflow from the gas/liquid separator too high - sample vapor being pumped out with the liquid.	Adjust the flow.
	Outflow from the gas/liquid separator too low - liquid escaping into the sample transfer tube.	Adjust the flow. Dry the sample transfer tube or fit a new one.
	Membrane wet.	Install a new dry membrane. Use Anti-foaming Agent in samples if problem continues.
	Gas/liquid separator contaminated.	Clean the gas/liquid separator.
	Carrier Gas Flow Flow of carrier gas not suitable.	Optimize the carrier gas flow.

Fluid Flows, Leaks, Blockages, Contamination

Carrier or reductant flows are wrong. Ration of flows not 2:1.	Make sure that the carrier and reductant tubes are in the correct containers. Set the flows correctly.	
	Worn pump tubes.	Replace any worn pump tubes.
	Leaks in the fluid system.	Make sure that all the tube connections are tight. Tighten them by hand and replace any damaged connectors.
	Contaminated fluid system.	Clean the fluid system. (See 10.2.1)
	Manifold blocked.	Clean the manifold. (See 10.2.1)
	FIMS-Cell	
	Cell windows or inner surface of cell may require cleaning.	Clean the cell or windows. (See 10.2.3)
	Sample is being extracted too quickly from the cell, reducing the residence time of the sample.	Reduce the extraction rate of fumes from the exhaust outlet of the cell.
All replicates following the first reading give low absorbance reading.	Fill step in FIAS program too short.	Increase the time for the Fill step on the FIAS page of the Method Editor.
The first replicate of a series gives low absorb	reading.	Prefill step in FIAS programs too short.

Increase the time for the	Prefill step on FIAS page of the Method Editor, or shorten	the tube between the sample container and the FIAS-valve.
Double peak in peak display	Concentration of samples too high.	Dilute the samples.
	Air trapped in the fluid system.	Make sure that all the tube connections are tight. Tighten them by hand and replace any damaged connectors.
	Carrier or reductant flows are wrong. Ratio of flows not 2:1.	Make sure that the carrier and reductant tubes are in the correct containers. Set the flows correctly.
Baseline shift in Peak Profile	Air trapped in fluid system.	Make sure that all the tube connections are tight.

11.2 Problems With the Instruments:

Problem	Possible Cause	Check/Remedy
FIMS	FIMS not switched on.	Switch on the system as described in section 9.4.
	Communication cable connection loose. Wrong interface or parameter-setting in the **HARDWARE.INI** file.	Make sure that the cables are correctly connected.
Select the correct interface (IEEE) in the **HARDWARE.INI** file and enter the correct parameter-settings for the interface. FIMS	and the autosampler must have identical parameter-settings.	Autosampler will not function